Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Metal-Induced Dimensionality Tuning within Bipyrimidine-based Chromophores: A Tool to Enhance Two-Photon Absorption

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Figure S1 Solvatochromic plots of Stokes shift for the chromophores.

Figure S2 Time fluorescence decays of the chromophores recorded at their respective λ_{fluo}^{MAX}; instrumental response function (IRF). Residual graphs relative to single-exponential fits. (solvent : DCM)

Figure S3 Job plots for complexation of the ligands with Zn^{2+}, based on the maximum fluorescence changes of the chromophores in THF. For each titration curve $[Li]+[Zn^{2+}] = 2x10^{-5}$ M. The full lines are provided as a guide to the eye.

Table S1 The crystal and structure refinement data of **L1**-complex.

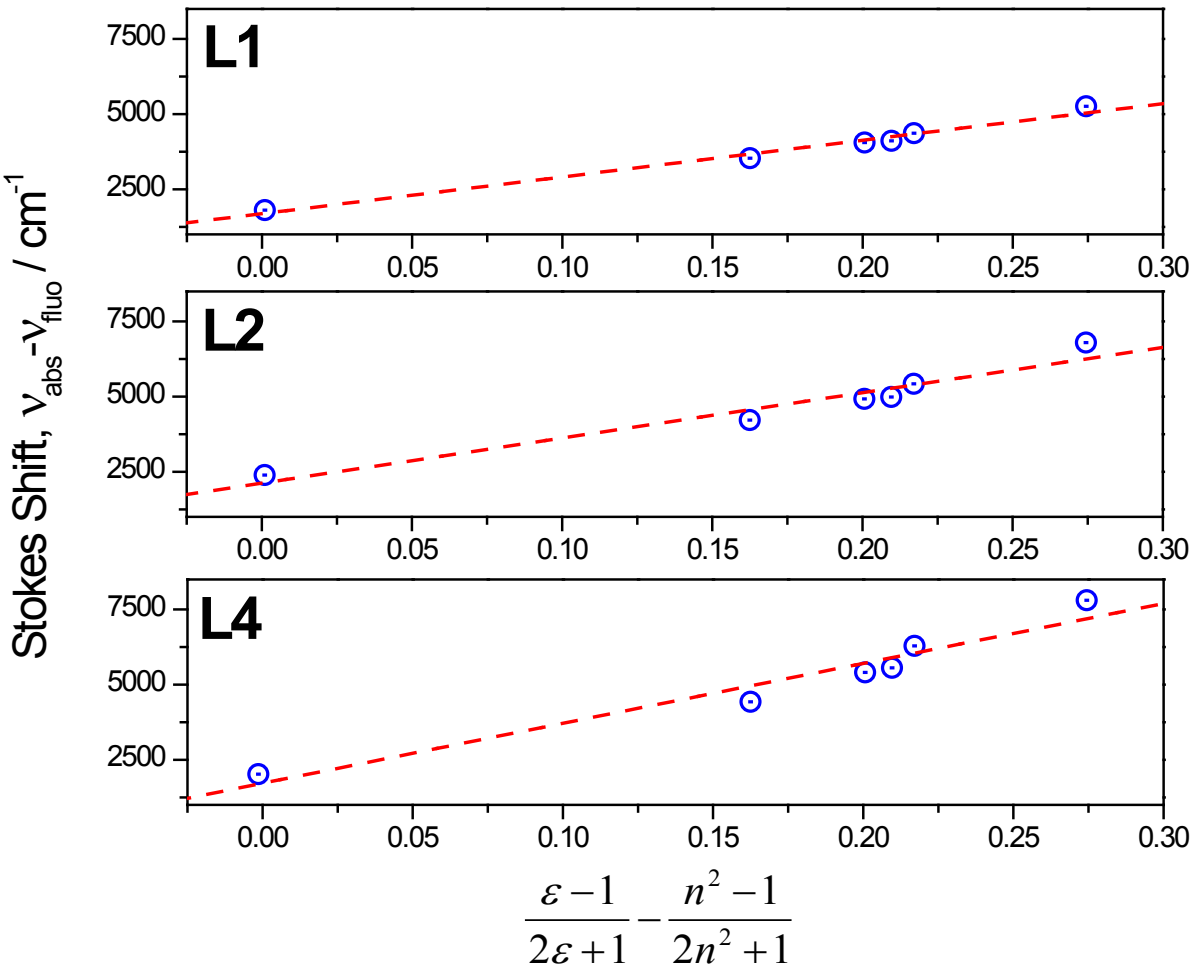

Figure S1.

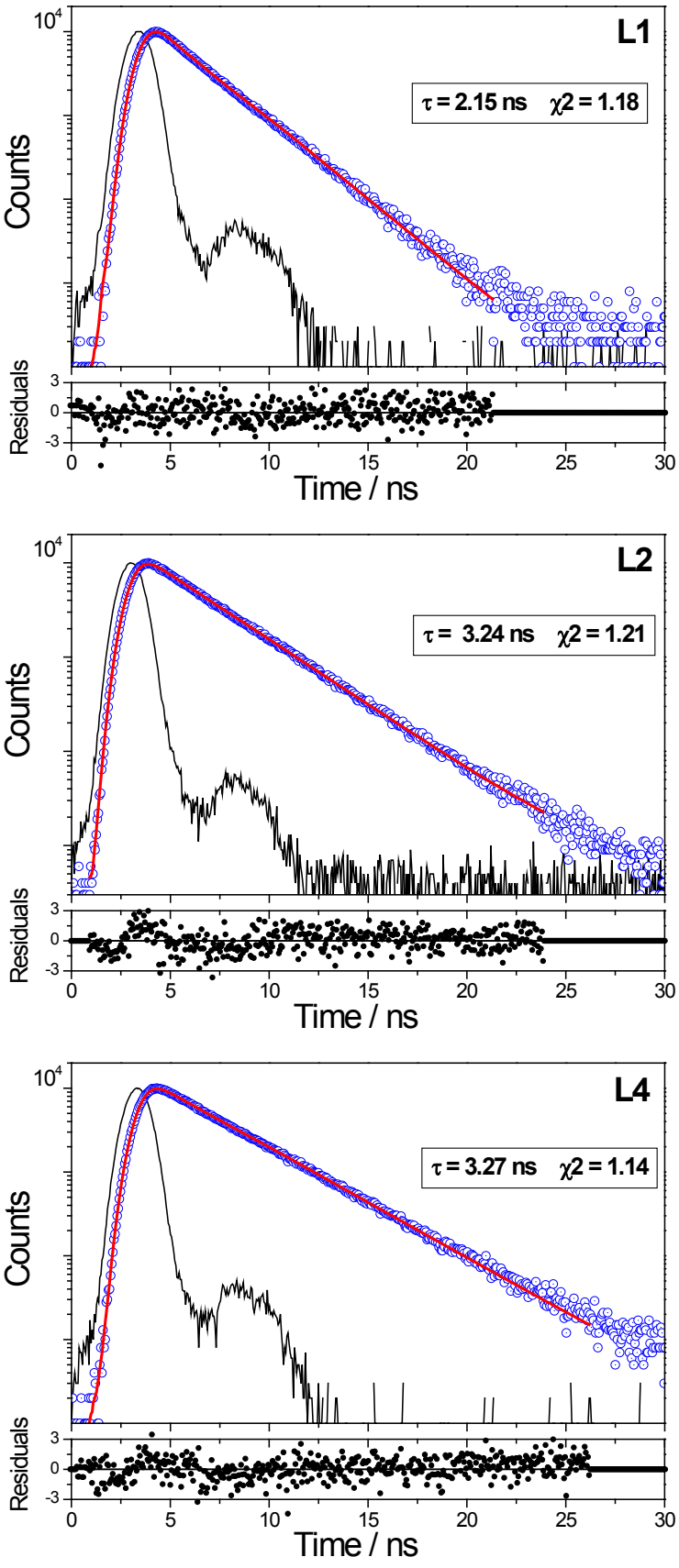

Figure S2.

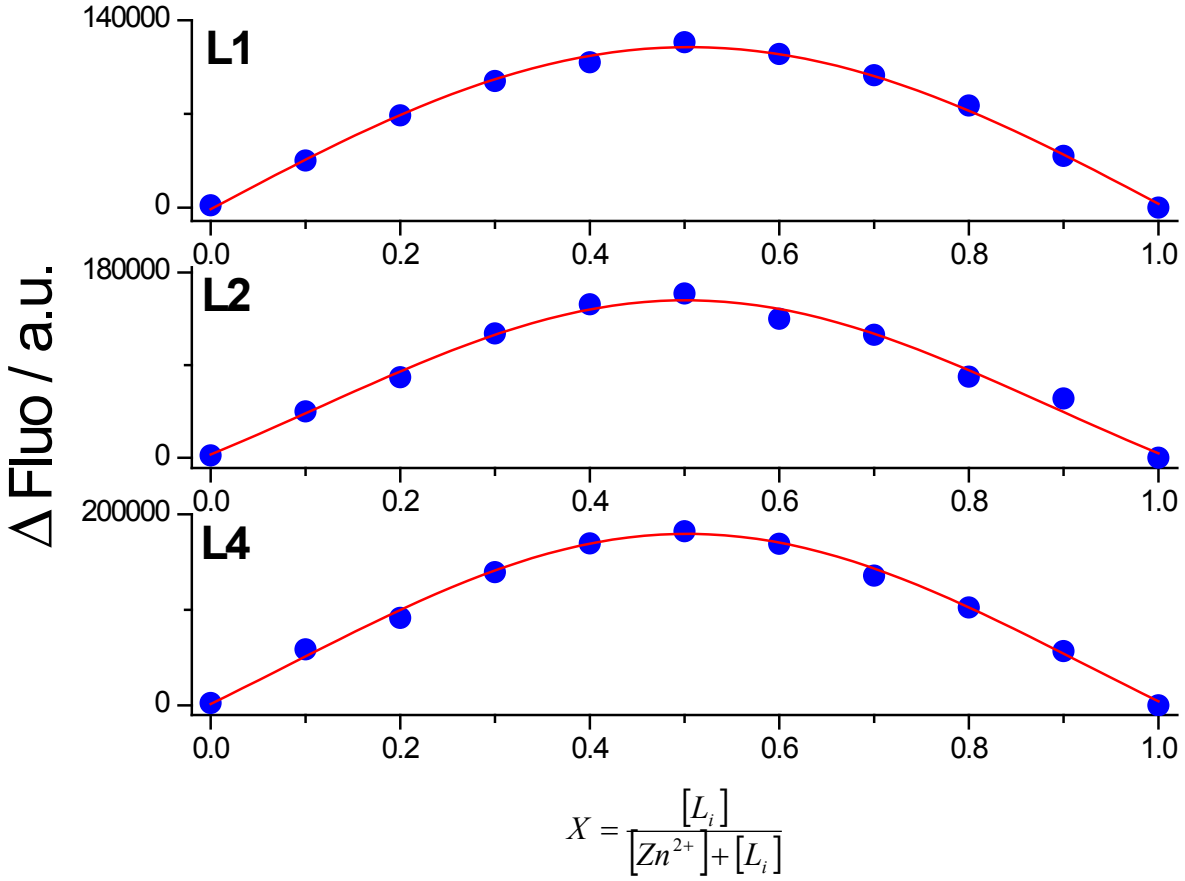

Figure S3.

Table S1 The crystal and structure refinement data of **L1**-complex.

X-ray crystallographic study

(C_{60} H_{68} Cl_2 N_4 Zn); M = 981.45. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 100(2) K; monoclinic *C2/c* (I.T.#15), a = 27.239(3), b = 26.022(3), c = 15.3824(15) Å, β = 101.558(6) °, V = 10682(2) Å^3, Z = 8, d = 1.221 g.cm^{-3}, μ = 0.601 mm^{-1}. The structure was solved by direct methods using the *SIR97* program [1], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*) [2] with the aid of the *WINGX* [3] program. The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm [4], implemented as the *SQUEEZE* option in *PLATON* [5]. A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 12142 unique intensities and 451 parameters converged at ω$R(F^2)$ = 0.3045 ($R(F)$ = 0.1049) for 4847 observed reflections with $I > 2\sigma(I)$.

[1] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. (1999) 32, 115-119
[2] Sheldrick G.M., Acta Cryst. A64 (2008), 112-122
[3] L. J. Farrugia, J. Appl. Cryst., 1999, 32, 837-838
[4] P. v.d. Sluis and A.L. Spek, Acta Cryst. (1990) A46, 194-201
[5] A. L. Spek, J. Appl. Cryst. (2003), 36, 7-13

Structural data

Empirical formula	C_{60} H_{68} Cl_2 N_4 Zn
Formula weight	981.45
Temperature	100(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *C 2/c*
Unit cell dimensions	a = 27.239(3) Å, α = 90 ° b = 26.022(3) Å, β = 101.558(6) ° c = 15.3824(15) Å, γ = 90 °
Volume	10682(2) Å^3
Z, Calculated density	8 , 1.221 (g.cm^{-3})
Absorption coefficient	0.601 mm^{-1}
F(000)	4160
Crystal size	0.4 x 0.12 x 0.09 mm
Crystal color	dark red
Theta range for data collection	3.41 to 27.45 °
h_min, h_max	-34 , 35
k_min, k_max	-33 , 33
l_min, l_max	-19 , 17
Reflections collected / unique	52855 / 12142 [R(int) = 0.0723]
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max. and min. transmission	0.947 , 0.725
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12142 / 0 / 451

Goodness-of-fit	1.005
Final *R* indices [I>2σ]	$R1^a$ = 0.1049, $wR2^b$ = 0.3045
R indices (all data)	$R1^a$ = 0.2031, $wR2^b$ = 0.354
Largest diff. peak and hole	1.317 and -0.844 e.Å^{-3}

$^{a}R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

$^{b}wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$